Glass and Ceramics, Vol. 69, Nos. 11 – 12, March, 2013 (Russian Original, Nos. 11 – 12, November – December, 2012)

COATINGS

UDC 666.1.058.1:666.28

OPAQUE PAINTS BASED ON A WATER EMULSION OF ÉD-20 RESIN FOR DECORATING GLASS ARTICLES

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Translated from *Steklo i Keramika*, No. 11, pp. 28 – 31, November, 2012.

It is shown that water epoxy emulsions can be used as a binder to obtain paints for decorating glass articles. The physical-chemical properties of epoxy coatings are studied.

Key words: epoxy emulsion, hardener, chemical stability, adhesion, hardness.

The production of glass articles is increasing worldwide. Their assortment is expanding and the operating and aesthetic properties are improving. Naturally, many customers strive to make them interesting and individual. Decoration of glass is ideal for such purposes. Decorative coloring of bottles, perfume bottles and assorted glassware are widely available abroad. A colored container makes the product easy to recognize, and its attractive appearance makes it possible to offer it at a higher price level. Colored bottles enable producers to protect their product from counterfeiting, which is an important competitive advantage over unprotected brands.

The conventional method of decorating glass articles is to deposit on their outer surface fired, low-melting, lead-containing enamels, which cannot harm anyone using the decorated articles because the lead compounds present in the enamel coatings are strongly bound. However, there are concerns at the production stage of these enamels. In sections where batch based on lead oxide is loaded and melted a fine powder is prepared for enamels, the content of lead compounds in air can be higher than the maximum admissible concentrations. According to the operative regulations SanPiN 13-3 RB 01 the maximum admissible amount of lead in the air in the working zone must not exceed 0.02 mg/m^3, while 0.03 mg/m^3 of lead are released from decorative coatings during sanitary-chemical tests of glass articles.

At the present time, according to a European Parliament Directive No. 2004/42/ES all painting materials (PM) must not harm human health or the environment at the production stage and during use. To be competitive in the European Union the domestic producers must change the recipe and technology used to produce PM so as not to raise any questions among environmentalists. An alternative, for example, to the production of lead-containing enamels can be the production of lead-free enamels, which possess a quite wide range of colors and quality in no way inferior to that of lead enamel coatings [1, 2].

The drawbacks of the conventional firing method of decoration are high energy-intensiveness of the process and high cost of production. In addition, the firing temperature of the decorated articles is dangerously close to the softening temperature of glass, which complicates the selection of the treatment temperature and often results in deformation of the decorated articles.

Modern production of artistic glass articles requires unconventional methods of decoration using new environmentally safe non-fired materials with high weather resistance. Water emulsions (WE) of epoxy resins (ER), whose main advantages over organic analogues are environmental safety, lack of organic solvents, water solubility, and fire and explosion resistance. For example, it is known that the use of WE of ER as a binder for obtaining compositions for protecting preserved-food containers from corrosion [3], ferrous metals [4] and so on. However, there are no data in the literature on the use of water epoxy emulsions in prescriptions for paints to be used for decorating glass or on research concerning the physical-chemical properties of coatings based on them.

The objective of the present work was to obtain unfired water-soluble epoxy paints for decorating glass and determining the physical-chemical properties of coatings based on them.

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The paints developed for decorating glass comprised compositions consisting of two parts, mixed immediately before application. One part (*component A*) included a pigment and the second part (*component B*) a hardener comprised a 55% water emulsion of a polyamine adduct (Epilink701, produced in the USA) in whose presence the most complete cross linking of epoxy coatings based on ÉD-20 WE of ER was observed [4]. A water emulsion of ÉD-20 resin modified beforehand with tetrabuthoxysilane [5] was used for the binding agent. Titanium dioxide and kaolin served as the pigment and filler, respectively.

These studies lead to the development of the base composition of white paint (wt.%): 30 – 40 WE of ER; 8 – 13 TiO_2, 5 – 30 kaolin, 1 – 2 process additive; and, distilled water. It was determined that coatings with finish varying from matte to lustrous can be obtained by varying the amount of kaolin. Inorganic colorants from the Eurocolori S.r.I. (Italy), added to the base paint in amounts 2 – 7 wt.%, were used to prepare colored paints. After the pastes were introduced the mixture was carefully mixed for 30 – 45 min to obtain a uniform state. Paints ranging from pastels to saturated tones were obtained depending on the amount of colorant introduced. The paints were mixed with one another in definite proportions in order to obtain paints with a wider range of color tones. There are a number of technological advantages to using inorganic coloring pastes. These coloring pastes are distinguished by the stability and intensity of the color tone, dispersity, viscosity, density, resistance to UV radiation and action by atmospheric factors and chemical stability.

Before paints are applied to a glass surface two components (*A* and *B*) were mixed together until fully blended. Paint consistency was regulated by varying the amount of water depending on the required method of application (pouring, brushing, spraying or dipping). The conventional viscosity of the finished paints, determined with a VZ-4 viscosimeter, was 15 – 35 sec and the spreadable life 80 – 90 min. The paints were applied on 30 × 30 × 2.5 mm sodium-calcium-silicate glass plates. The optimal thickness of the coatings was 20 – 60 μm. The coatings were allowed to dry at temperature 20 ± 2°C. The time to degree-3 drying (to tackiness) at 20 ± 2°C is 1 h.

The technical level of quality of the decorated articles largely depends on their reliability. The operational reliability of these articles is one of the most important quality indicators, which is characterized by the service life or durability as well as shelf life. The resistance of decorative coatings to the action of external media (durability) is usually evaluated by the following indicators: chemical stability, hardness and coating – substrate adhesion [6].

The chemical stability of the coatings was determined by a procedure developed in the Laboratory of Art Glass at the Gusev Affiliate of the State Scientific-Research Institute of Glass [7]. The method is based on controlling the mass change of the sample on 100 cm^2 of a paint coating after treatment with reagent solutions. The samples were kept for 2 h in distilled water and 2% solution of sodium carbonate at 98 ± 2°C and for 30 h in the same reagents at 20 ± 2°C. The amount of reagent was taken to be 5 cm^3 per 1 cm^2 surface area of the sample. The sample mass change *a* (%) per 100 cm^2 surface area coated with paint was determined from the relation

$$a = \frac{m - m_1}{S} \times 100a,$$

where m and m_1 are, respectively, the mass of the glass sample coated with paint before and after exposure to the reagent, mg, and S is the sample surface area coated with paint, cm^2.

The mass losses of the samples with an unpainted surface can be neglected, because they are negligible and fall within the measurement error.

The hardness of the coatings was determined with a 2124 TML pendulum instrument following GOST 5233; the adhesion of the decorative coatings to the substrate were determined by the detachment method using the Adgezimetr OR apparatus in accordance with ISO 4624 and the elasticity (strength under conical bending) according to GOST 6806–73 using the KONSTANTA IK apparatus by bending a film deposited on a tin plate, round a metal rod with various diameters until cracks appear. In this method the shortest diameter of a rod on which bending of the colored metal plate does not damage the paint coating is determined.

An IR-spectrometer with M 2000 Series FTIR SPECTROMETER with Fourier transformation (MIDAC Company, USA) was used to obtain the IR spectra of the samples in the wavelength range 400 – 4000 cm^{-1} with resolution 4 cm^{-1}. The spectra were acquired using the Grams/32 computer program (Galactic Company, USA).

It should be noted that the most suitable absorption band of the epoxy group for studying chemical transformations of ER is the band peaking at 910 cm^{-1}; all other bands overlap with other absorption bands [8]. Since in the course of solidification epoxy resins interact with an amine functional group of hardeners the absorption intensity near 910 cm^{-1} can serve as a measure of the chemical conversion of the process. In the course of the solidification of the experimental paints by the hardener Epilink 701 over 2 days an absorption band peaking at 910 cm^{-1} is observed, indicating the presence of epoxy groups and incomplete cross-linkage. Increasing the drying time of the coatings at room temperature to 10 days results in complete cross linking of the epoxy groups; this is indicated by the absence of absorption bands peaking at 910 cm^{-1} in the IR spectra.

The investigations showed that the hardness of the coatings formed at 20°C in 2 days is too low (0.13 – 0.14 arb. units), but as the hardening time increases it increases noticeably. Coatings acquire their greatest hardness after they harden over 10 days (H = 0.32 – 0.35 arb. units), i.e., the time required for complete stabilization (cross linking) of the epoxy system.

TABLE 1. Chemical Stability of Paint Coatings

Paint color	Mass increment of a decorative coating after exposure to chemical reagents, g (per 100 cm^2 surface area)			
	distilled water		2% soda solution	
	at 20 ± 2°C for 30 h	at 98 ± 2°C for 2 h	at 20 ± 2°C for 30 h	2% soda solution at 98 ± 2°C for 2 h
White	0.00286	0.00387	0.00133	0.00344
Yellow	0.00285	0.00395	0.00135	0.00348
Green	0.00288	0.00391	0.00134	0.00346
Black	0.00289	0.00388	0.00131	0.00349

TABLE 2. Comparative Characteristics of the Adhesion of Epoxy Compositions to a Glass Substrate with a 2 mm Thick Glue Line

Paint color	Peel strength, MPa				
	before testing	after exposure to chemical reagents			
		distilled water		2% soda solution	
		at 20 ± 2°C for 30 h	at 98 ± 2°C for 2 h	at 20 ± 2°C for 30 h	at 98 ± 2°C for 2 h
White	3.87	3.16	2.15	3.59	2.73
Yellow	3.89	3.18	2.18	3.58	2.76
Green	3.91	3.20	2.22	3.61	2.67
Black	3.93	3.22	2.24	3.63	2.69

Elasticity determines the capability of a paint film to re-acquire its previous shape after the deforming force is removed. Studies have shown that our compositions are quite elastic, since they remain undamaged after bending on a 3 mm in diameter rod.

The results of tests of the capability of paint coatings to resist certain chemical media are presented in Table 1.

The tabulated data show that the coatings show a small mass increase irrespective of the color after exposure to the reagents indicated above. The coatings retain their integrity and color and show no traces of cracks, bubbles or separation from the glass substrate. With regard to chemical stability the glass articles decorated with the new paints are fully competitive with analogous articles decorated with organic acrylic epoxy paint with coating drying temperature 170°C [9].

The adhesion values at detachment of decorative coatings to a glass substrate before and after tests in chemical reagents are presented in Table 2.

It is evident from that data presented in Table 2 that epoxy paints possess good adhesion. It should be noted that after the tests cohesion separation from parts of the glass substrate is observed on all samples, which attests to good adhesion of the paints to the base.

In summary, new compositions have been developed for unfired, environmentally full-value, epoxy paints for obtaining decorative coatings on glass with different surface texture based on an epoxy emulsion of ÉD-20 resin. The new paints will make it possible to respond quickly to customer inquiries.

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